Isotope Effect in Rattling-Induced Superconductor

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The Bardeen-Cooper-Schrieffer (BCS) theory for superconductivity[1)] has been proved by several kinds of experiments. Among them, the isotope effect on superconducting transition temperature $T_{\rm c}$ has been one of key experiments for the BCS theory. If the Cooper pair is formed by phonon-mediated attractive interaction, $T_{\rm c}$ should be determined by a characteristic phonon energy ω, which is related to the mass of oscillator M as $\omega \propto M^{-1/2}$. When we express the relation between $T_{\rm c}$ and M as

$$T_{\rm c} \propto M^{-\eta}, \tag{1}$$

we obtain $\eta = 1/2$ for BCS superconductors mediated by phonons. In actual experiments on Hg,[2,3)] it has been clearly shown that $T_{\rm c}$ is in proportion to $M^{-1/2}$, leading to the evidence of phonon-mediated Cooper pair. Note, however, that in Ru,[4)] the value of η has been found to be smaller than $1/2$. This is understood by the effect of Coulomb interaction in the famous McMillan formula.[5)]

Recently, phonon-mediated superconductivity has attracted renewed attention from a viewpoint of *anharmonicity* since the discovery of superconductivity with relatively high $T_{\rm c}$ in β-pyrochlore oxides.[6–9)] From both experimental and theoretical efforts,[10–14)] it has been gradually recognized that the superconductivity is induced by anharmonic oscillation of alkali atom contained in a cage composed of oxygen and osmium. Such anharmonic oscillation is called *rattling* and it is highly believed that the rattling plays a crucial role for the emergence of superconductivity in cage compounds.

In this paper, we evaluate the exponent η within the weak-coupling BCS theory for rattling-induced superconductor. It is shown that η becomes larger than $1/2$, indicating anomalous isotope effect. We also find that η increases with the increase of the amplitude of guest ion, which is relevant to β-pyrochlore oxides. We propose an experiment on the isotope effect in order to prove a key role of rattling in β-pyrochlore oxides. We emphasize that the increase of η more than $1/2$ is first reported in this paper, although the decrease of η less than $1/2$ has been understood by the effect of Coulomb interaction. Throughout this paper, we use such units as $\hbar = k_{\rm B} = 1$.

We consider the Holstein model, given by

$$H = \sum_{\boldsymbol{k},\sigma} \varepsilon_{\boldsymbol{k}} c^{\dagger}_{\boldsymbol{k}\sigma} c_{\boldsymbol{k}\sigma} + H_{\rm loc}, \tag{2}$$

where $\boldsymbol{k}$ is momentum of electron, $\varepsilon_{\boldsymbol{k}}$ denotes the energy of conduction electron, σ is an electron spin, $c_{\boldsymbol{k}\sigma}$ is an annihilation operator of electron with $\boldsymbol{k}$ and σ, $H_{\rm loc}$ denotes local electron-vibration term, expressed as

$$H_{\rm loc} = g \sum_{\boldsymbol{i},\sigma} Q_{\boldsymbol{i}} c^{\dagger}_{\boldsymbol{i}\sigma} c_{\boldsymbol{i}\sigma} + \sum_{\boldsymbol{i}} [P_{\boldsymbol{i}}^2/(2M) + V(Q_{\boldsymbol{i}})]. \tag{3}$$

Here g is electron-vibration coupling constant, $\boldsymbol{i}$ denotes atomic site, $c_{\boldsymbol{i}\sigma}$ is an annihilation operator of electron at site $\boldsymbol{i}$, $Q_{\boldsymbol{i}}$ is normal coordinate of the oscillator, $P_{\boldsymbol{i}}$ indicates the corresponding canonical momentum, M is mass of the oscillator, and V denotes an anharmonic potential for the oscillator, given by $V(Q_{\boldsymbol{i}}) = M\omega^2 Q_{\boldsymbol{i}}^2/2 + k_4 Q_{\boldsymbol{i}}^4 + k_6 Q_{\boldsymbol{i}}^6$. Here ω is energy of oscillator, while k_4 and k_6 are the coefficients for fourth- and sixth-order anharmonic terms.

By using the phonon operator $a_{\boldsymbol{i}}$ defined through $Q_{\boldsymbol{i}} = (a^{\dagger}_{\boldsymbol{i}} + a_{\boldsymbol{i}})/\sqrt{2M\omega}$ at site $\boldsymbol{i}$, we obtain

$$\begin{aligned} H_{\rm loc} = \sqrt{\alpha}\omega \sum_{\boldsymbol{i},\sigma} (a_{\boldsymbol{i}} + a^{\dagger}_{\boldsymbol{i}}) + \omega \sum_{\boldsymbol{i}} [a^{\dagger}_{\boldsymbol{i}} a_{\boldsymbol{i}} + 1/2 \\ + \beta (a_{\boldsymbol{i}} + a^{\dagger}_{\boldsymbol{i}})^4 + \gamma (a_{\boldsymbol{i}} + a^{\dagger}_{\boldsymbol{i}})^6], \end{aligned} \tag{4}$$

where $\alpha = g^2/(2M^2\omega^3)$, $\beta = k_4/(4M^2\omega^3)$, and $\gamma = k_6/(8M^3\omega^4)$. With the use of non-dimensional parameters α, β, and γ, it is convenient to rewrite V as

$$V(q_{\boldsymbol{i}}) = \alpha\omega (q_{\boldsymbol{i}}^2 + 16\alpha\beta q_{\boldsymbol{i}}^4 + 64\alpha^2\gamma q_{\boldsymbol{i}}^6), \tag{5}$$

where $q_{\boldsymbol{i}}$ is non-dimensional displacement, defined by $q_{\boldsymbol{i}} = Q_{\boldsymbol{i}} M\omega^2/g$.

Here we define the M dependence of parameters.[15)] It is well known that the phonon energy ω is in proportion to $M^{-1/2}$ from $\omega = \sqrt{k/M}$ with a spring constant k, when we assume that k dose not depend on M. If we further assume that g is independent of M, we obtain $\alpha \propto M^{1/2}$. Note that $\alpha\omega$ does not depend on M. Concerning anharmonic parameters β and γ, we obtain that $\beta \propto M^{-1/2}$ and $\gamma \propto M^{-1}$ by assuming that k_4 and k_6 are independent of M. Hereafter, we explicitly consider m dependence of parameters as $\omega = \omega_0/\sqrt{m}$, $\alpha = \alpha_0\sqrt{m}$, $\beta = \beta_0/\sqrt{m}$, and $\gamma = \gamma_0/m$, where m indicates the mass ratio of the guest ion.

Now we consider the M dependence of the superconducting transition temperature $T_{\rm c}$, given in the BCS theory by

$$T_{\rm c} = 1.13\omega e^{-1/\lambda}, \tag{6}$$

where $\lambda = U_{\rm ph}/W$, $U_{\rm ph}$ is the phonon-mediated attraction, and W is the electron bandwidth. The exponent η in the isotope effect is evaluated by $\eta = -d\log T_{\rm c}/d\log m$, leading to

$$\eta = \frac{1}{2} - \frac{m}{\lambda^2}\frac{d\lambda}{dm}. \tag{7}$$

Note that for a harmonic case with $\beta_0 = \gamma_0 = 0$, we obtain $\lambda = 2\alpha\omega/W = 2\alpha_0\omega_0/W$, which does not depend on M. Thus, we find $\eta = 1/2$ for the harmonic case (normal isotope effect). However, for anharmonic phonons, $U_{\rm ph}$ depends on M and the value of η is deviated from $1/2$. In the following calculations, we set W=1 as an energy unit.

First we show the anharmonic potentials considered in this paper. In Fig. 1(a), we show potentials for several values of β'_0 with $\gamma_0 = 10^{-4}$, $\omega_0 = 0.05$, and $\lambda_0 = 2\alpha_0\omega_0 = 0.5$, where $\beta'_0 = \beta_0/\sqrt{\gamma_0}$. As already mentioned in our previous paper,[14)] the potential shapes are classified into three types: On-center type for $\beta'_0 > -\sqrt{3}/2$, rattling-type for $-1 < \beta'_0 < -\sqrt{3}/2$, and off-center type $\beta'_0 < -1$.

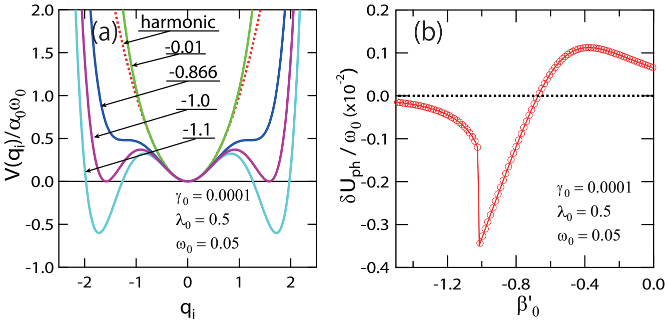

Fig. 1. (Color online) (a) Anharmonic potentials for β'_0=-0.1, -0.866, -1.0, and -1.1. Dotted curve denotes harmonic potential. (b) Variation of attraction $\delta U_{\rm ph}/\omega_0$ as a function of β'_0 for m=1.01.

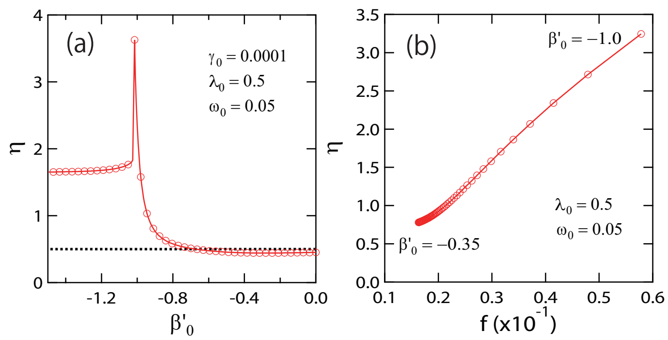

Fig. 2. (Color online) (a) Exponent η vs. β' for γ=10^{-4}, λ=0.5, and ω = 0.05. Dotted line indicates η=1/2 for the normal isotope effect. (b) Exponent η vs. Debye-Waller factor f. Note that the anharmonicity increases with the increase of f.

Next we show that $U_{\rm ph}$ is actually changed by M for the case of anharmonic oscillation. For the purpose, we evaluate the magnitude of $U_{\rm ph}$ as

$$U_{\rm ph} = 2E_1^{(0)} - (E_2^{(0)} + E_0^{(0)}), \tag{8}$$

where $E_n^{(0)}$ is the ground-state energy of $H_{\rm loc}$ for local electron number n. In Fig. 1(b), we depict $\delta U_{\rm ph}/\omega_0$ as a function of β'_0 for γ_0=10^{-4}, λ_0=0.5, and ω_0=0.05, where $\delta U_{\rm ph}$ is estimated by $\delta U_{\rm ph} = U_{\rm ph}(m = 1.01) - U_{\rm ph}(m = 1)$. For the diagonalization of $H_{\rm loc}$, we use 250 phonon basis. Note that $\delta U_{\rm ph}$=0 for the harmonic case. We find that the attraction mediated by anharmonic phonons is significantly affected by M.[15] In particular, for the on-center type potential, $U_{\rm ph}$ is increased by the increase of M, while it is decreased for rattling and off-center type potentials for γ_0=10^{-4}.

Now we move to the result of η. In Fig. 2(a), we show η as a function of β'_0 for γ_0=10^{-4}, λ_0=0.5, and ω_0=0.05. Note that in the actual calculation, we evaluate $d\lambda/dm$ from $\delta U_{\rm ph}/0.01$. For $\beta'_0 > -0.8$, we find the normal isotope effect with $\eta \approx 0.5$, but in the region of $-1.0 < \beta'_0 < -0.8$ corresponding to the rattling-type potential, we find sharp increase of η. In the off-center type potential for $\beta'_0 < -1.0$, we find that η is moderately enhanced.

Here we focus on the region of $-1.0 < \beta'_0 < 0$ in order to discuss possible relevance of the present result with the isotope effect of β-pyrochlore oxides AOs_2O_6 (A = K, Rb, and Cs). When alkali ion radius is decreased in the order of Cs, Rb, and K, the amplitude of the oscillation of alkali ion is increased, since the anharmonicity in the potential is increased in the order of Cs, Rb, and K.[11] Here we introduce the Debye-Waller factor f in a non-dimensional form as $f = \langle Q_i^2 \rangle / 3\ell^2$, where $\ell = g/k$ and $\langle \cdots \rangle$ denotes the operation to take thermal average. In Fig. 2(b), we show η vs. f, where f is evaluated at $T = 0.01$, corresponding to a room temperature. Here we change anharmonic parameter set (β, γ) from $(-0.0253, 0.00451)$ for β'_0=-0.35 and A=Cs to $(-0.0392, 0.00154)$ for β'_0=-1.0 and A=K, which have been determined to reproduce the Debye-Waller factors for AOs_2O_6.[14] The anomalous isotope effect with $\eta > 1/2$ is expected to occur in β-pyrochlore oxides. We predict that the value of η is increased in the order of Cs, Rb, and K.

In this paper, we have evaluated η for rattling-induced superconductor on the basis of the BCS formula in the weak-coupling limit. As shown in our previous study, the strong-coupling effect is significant in the rattling-induced superconductivity when the anharmonicity is increased. Thus, in order to discuss η in more detail, it is necessary to calculate precisely $T_{\rm c}$ as well as the renormalization factor by changing M within the Eliashberg theory. It is our future task.

In summary, we have proposed that the isotope effect with the exponent $\eta > 1/2$ is found in the superconductivity due to electron-rattling interaction. The detect of this anomalous isotope effect can be the evidence of superconductivity induced by rattling in β-pyrochlore oxides.

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